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**CERTIFICATE OF TRANSLATION**

I, the undersigned do hereby certify that to the best of my knowledge and belief the following is a true and accurate translation into English of the German-language document identified as 224-53 (D4695-00132).

Signed on this 17th day of May, 2005.



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41 PCT

Fraunhofer Gesellschaft ... e.V.  
11168p; Specification

**Process for Manufacturing Coated Expanded Metals and Use of Such Metals as Current Collectors in Electrochemical Components**

5 The present invention pertains to a process for manufacturing coated expanded metals, which are suitable for use, among other things, as current collectors in electrochemical components, especially in nonaqueous electrochemical cells.

10 Typical representatives of nonaqueous electrochemical cells are lithium batteries. These have been known in various embodiments for a long time and have been described several times. The design of these cells is as follows: An anode, either one consisting of lithium metal or graphite, is arranged opposite a cathode, usually a stable lithium interstitial compound. The two electrodes are separated by a separator. The complete system is interspersed by an electrolyte, which establishes the ionic conductivity for lithium ions. They are formed, as a rule, by a lithium salt dissolved in one or more organic solvents. Lithium ions move to and fro between the electrodes during charging and discharging.

15 To avoid the problem of unbound electrolyte liquids inside the battery body, successful attempts were made at making the electrodes and the separator in the form of foils. These foils are characterized either by a high microporosity, in which the liquid electrolyte is immobilized, or by the addition of suitable polymers, which form a gel with the liquid.

20 Besides the electrochemical components described, such components require current collectors to collect and drain off the electron current and make it usable for the user. The current collectors are metals, which are introduced either as foils or as expanded metals. They shall meet a number of conditions, namely, (a) they must be electrochemically stable against corrosion, (b) they shall have good contact with the particular electrodes to ensure a low contact resistance, (c) they shall have a low weight in order to guarantee high energy densities, and (d) they shall have favorable elastic properties in order to compensate variations in volume during the intercalation and de-intercalation of lithium ions in the electrodes during the operation. Aluminum and graphite have proved to be suitable for use as metals that are stable in the electrochemical environment of the battery for the system used commonly with lithium cobalt oxide as the cathode material and graphite on the anode side. However, the process being described here is not limited to these metals.

25 30 35 40 The manufacture of expanded metals shall be briefly explained below. The process is schematically shown in Figure 1. Metal foils (1) of a suitable thickness are provided with a punched pattern in a punching tool (2) and then stretched (3). The geometric data of the expanded metal, such as the width of the web, the opening diagonals and the percentage of open area are set by designing the punched pattern and the rate of stretching.

45 The advantages of the use of expanded metals as current collectors are obvious: Compared to foils, they have an open-pore structure, so that the weight of the current collectors can be reduced, which entails advantages in the gravimetric energy density. In addition, the expanded metal is elastic in such a way that it can follow the changes in volume during the intercalation and

de-intercalation of lithium in the electrodes, without delamination taking place. Delamination would in turn reduce the cycle life of the batteries.

- 5 Another advantage is achieved in terms of production engineering when expanded metal is used in lithium-polymer batteries. This type of battery is usually manufactured as follows: The electrodes are either deposited directly on metal foils (see US 6,306,215) or are laminated on the current collector by lamination under pressure and optionally under the action of temperature (DE 199 52 335). A firm composite of the three different foils for the anode with the current collector, the separator and the cathode with the current collector is then prepared in a second step by lamination or by the winding technique. This composite is then impregnated with electrolyte liquid. The electrolyte liquid must be distributed uniformly in the complete foil composite. This is achieved essentially by capillary forces. This process is frequently also supported by the additional formation of pores, which are produced by adding a plasticizing agent to the electrode and separator materials, which is again removed by means of a solvent after the components have been laminated together. Closed metal foils make difficult the penetration of the liquid electrolyte into the battery body, i.e., they prolong the duration of the process. The use of an open-mesh expanded metal therefore offers considerable advantages in terms of process engineering.
- 20 To achieve good adhesion and low contact resistance at the interface between the metallic current collector and the laminated electrode, it proved to be advantageous to coat the current collector with a thin layer of adhesion promoter before it is connected to the electrode, and it is especially advantageous if the said adhesion promoter layer has an electron conductivity. A number of proposals have been made in the state of the art concerning the technique to be used to apply such adhesion promoters and their suitable compositions. They comprise the coating of current collectors made of expanded metals or of other perforated collectors (nettings, grids) in liquids or pastes by spin coating, dipping or coating (see US 6,306,215 and US 5,824,120), the application of a layer that contains carbon powder and an adhesiveness-improving polymer, by means of electrostatic forces (US 5,542,163), or a plasma polymerization method, by which a layer of an electrically conductive, polymeric, adhesion-improving material is applied to the current collector (see US 6,007,588). All the documents mentioned describe electrochemical cells from electrode materials with a plasticizing agent, which is again washed out of the cells after the individual components (electrode and separator layers or foils, current collector) have been laminated together in order to generate pore volume for the electrolyte liquid, as was described above. It is also possible to apply the coating by applying a suitable suspension by means of printing methods. Corresponding suspensions are commercially available. Methods based on the use of printing rollers, for example, reverse roll coating, are used. The suspensions consist, as a rule, of a carbon/polymer mixture in a suitable solvent, such as water.
- 30 Considerable problems arise in practical application when coating solutions are applied according to methods used in the printing trade. The layer thickness of the suspensions applied are usually between approx. 1 µm and approx. 20 µm. Insufficient wetting is invariably observed in the printing roller process, which leads to nonuniform distribution of the suspension on the metal. As a result, the contact resistance increases or contact is even lost between the current collector and the electrode at the poorly coated sites during the operation of electrochemical components equipped with expanded metals coated in this manner, e.g., batteries, and this has disadvantageous consequences for the service life of the components. However, the use of thicker adhesion promoter layers is ruled out because of the undesired reduction of the energy density that is associated with this.
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- Moreover, problems arise in terms of the hardware when printing methods are used to apply the adhesion promoter layers. To guarantee the precise guiding of the foils during coating, guiding of the metal foil over several deflecting rollers is necessary. In addition, the foil must be kept under a certain mechanical tension during its run through the coating machine. While this does not cause any technical problem in case of the use of closed metal foils, for example, foils made of aluminum or copper in case of foil thicknesses as low as approx. 10 µm to 15 µm, expanded metals tend to tear even under low tensile stresses. This is especially critical in case of aluminum expanded metals. Typical thicknesses of expanded metals are 50 µm or even less. Massive yield problems arise due to tearing even on machines designed especially for coating expanded metals.
- However, a changeover to thicker current collectors to improve the reliability of the process is just as impossible, because of an undesired reduction of the energy density, as coating with an excessively thick layer.
- The object of the present invention is to provide a process for manufacturing coated expanded metals, which leads to improved yields and with which the top side and the underside of thin expanded metals can also be coated with a sufficiently thin layer of conductive adhesion promoters.
- The said object is accomplished by a process in which a closed metal foil is first coated and this is then converted into expanded metal. This offers the advantage that the coating is applied to a mechanically substantially more stable metal foil, so that a product possessing the necessary properties can be manufactured with a high yield and the amount of rejects can be greatly reduced. Coating may be performed on one side or on both sides. It was quite surprising to find with this procedure that the coating applied to the foil does not flake off during stretching. This was not to be expected at all, because it was not possible to assume that it would be sufficiently elastic and, moreover, possess such a good adhesion that the deformation of the metal lying under the coating does not lead to separation of the coating.
- It was equally fully surprising that another advantage of the present invention was able to be observed, namely, that the service life of the punching knives increases during the manufacture of the expanded metal. This could be due to the fact that usual adhesion promoters are suspensions containing graphite, which act as lubricants for the knives during the punching operation and thus contribute to the prolongation of their service life.
- The present invention is explained in the attached drawings, in which
- Figure 1** shows the sequence of a laminate suitable for use for a battery,
  - Figure 2** shows the top view of such a laminate,
  - Figure 3** shows a schematic view of the manufacture of the expanded metal,
  - Figure 4** shows a diagram showing the relative capacity of a battery provided with an expanded metal manufactured according to the present invention as a collector, and
  - Figure 5** shows the relative capacity of a battery with an expanded metal manufactured according to the present invention as a collector compared to the capacity of a battery with a collector manufactured in the usual manner.

It is especially favorable if the metal foil is subjected to a corona discharge surface treatment already before the coating operation, because this measure leads to a further improvement in the adhesion of the coating on the expanded metal.

It is frequently preferred to stretch the metal during the expansion at most only to the extent that the short diagonal will have a length of about 1 mm and the long diagonal will have a length of about 2 mm because, depending on the flexibility of the coating materials used, the coating may separate in some cases when a greater stretching is carried out.

All the materials with which the desired properties that the expanded metal needs for its later use can be obtained are suitable for coating the metal foils that will subsequently be subjected to the expansion process. These are above all good adhesion to the electrodes as well as good electric conductivity in the case of expanded metals used as current collectors. However, it should be clear that the process according to the present invention is not limited to the manufacture of coated expanded metals for current collectors. It can rather be used wherever thin expanded metals with sensitive, thin coatings are to be used and it is not necessary that the openings generated during the punching and stretching also be coated laterally.

For example, materials such as graphite or other suitable carbon materials as well as adhesion-improving organic polymers shall be mentioned as suitable materials for coatings with good adhesion and good electric conductivity. The carbon materials may be applied in a binder, e.g., an organic polymer suspension, which binder can subsequently be dried, (after)cured or subjected to an additional polymerization on the surface. One example is EB-012 from the firm of Acheson, U.S.A., a graphite suspension, which contains a thermoplastic binder. Other examples are suspensions containing silver instead of graphite. The binders may be, e.g., epoxy resins, thermoplastics, duromers, vinyl resins, cellulose or fluoroelastomers. However, it is also possible to use other suitable materials instead of graphite suspensions if they impart the said properties, for example, electrically conductive organic polymers such as polyvinylpyrrolidone. Furthermore, polymer suspensions that are graphitized after the application to the metal are well suited for use as a coating.

The process according to the present invention was found in light of the poor quality of expanded metals coated according to the printing method. However, it is not limited to specific coating techniques. Instead of application according to the printing method, it is also possible to use, e.g., spin coating, roller coating, application with a doctor blade, dip coating, electrostatic application (powder coating) or the plasma method, as they are known, among other things, from the above-mentioned state of the art.

The expanded metals manufactured according to the present invention differ from the conventional ones by the fact that their openings, produced during the punching and stretching, are not coated laterally. However, this is of no disadvantage for their use as current collectors.

The expanded metals that are or can be manufactured according to the present invention are especially suitable, among other things, for use in electrochemical cells during the manufacture of which the addition of a plasticizer, which would have to be removed again in a subsequent washing process, to the electrode materials and/or the separator to produce a porosity necessary for taking up the liquid electrolyte is avoided, because this manufacturing process, which is described in the US patent specifications 5,456,000 and 6,063,519, requires, as an additional requirement on the adhesion promoter layer, that this layer be chemically stable in respect to the wash liquid. Partial separation of the electrode foils from the current collector may easily occur during the washing out of the plasticizer, which has unfavorable consequences for the cycle life and the impedance of a battery. It is therefore proposed according to the present invention as an

especially favorable solution that electrochemical components be manufactured with the current collectors manufactured according to the present invention, whose electrodes and separator were manufactured without a plasticizer that has to be washed out.

5 The present invention shall be explained in greater detail below on the basis of examples.

**Example 1**

**Copper Expanded Metal**

10 A copper foil with a thickness of 50 µm was coated on both sides with a commercially available suspension EB012 from Acheson Colloids B.V. (a thixotropic graphite suspension in a thermoplastic binder). To set the optimal viscosity for the application, the solids content in the suspension was reduced from 30% to 20% by adding water. Coating was carried out on one side by means of a simple laminating roller first on the front side and, in a second run, on the reverse side. The copper foil was a commercially available standard foil for use in batteries. The wet layer thickness applied was approx. 20 µm at a feed rate of 2.5 m/minute. Drying was carried out at approx. 80°C. The layer thickness of the adhesion promoter layer was still 4 µm after drying. The foil thus coated was subsequently subjected to further processing into expanded metal. Stretching was set such that the short diagonal had a length of 1 mm and the long diagonal had a length of 2 mm. The material obtained was free from separations and cracks in the metal and was able to be subjected to further use at a rate of 100%.

25 **Comparison Example 1**

Example 1 was repeated, and stretching was set such that the short diagonal had a length of 1.5 mm and the long diagonal had a length of 3 mm. There were cracks in the product; it was flaked off in some areas. The reject was about 30% of the area.

30 **Comparison Example 1a**

Example 1 was repeated such that the copper foil was first converted into expanded metal and this was coated as described. A large number of cracked areas and areas with flaked-off coating were found on the material obtained in a non-uniform distribution. Only one of 6 batches (rolls) was suitable for use in such a way that it was able to be used for the further processing of the expanded metal into current collectors. On the whole, more than 50% of the area of the expanded metal was damaged.

40 **Example 2**

**Aluminum Expanded Metal**

An aluminum foil with a thickness of 50 µm was coated on both sides with the above-mentioned, commercially available suspension EB012 from Acheson Colloids B.V. To set the optimal viscosity for the application, the solids content in the suspension was reduced from 30% to 20% by adding water. Coating was carried out by means of a simple laminating roller on one side, first on the front side and, in a second run, on the reverse side. The copper foil was a commercially available standard foil for use in

5 batteries. The wet layer thickness applied was approx. 20 µm at a feed rate of 2 m/minute. Drying was carried out at approx. 80°C. The layer thickness of the adhesion promoter layer was still 4 µm after drying. The foil thus coated was subsequently subjected to further processing into expanded metal. Stretching was set such that the short diagonal had a length of 1 mm and the long diagonal had a length of 2 mm. The material obtained showed no separations and cracks in the metal and was able to be used further at a rate of 100%.

### Comparison Example 2

10 Example 2 was repeated, and stretching was set such that the short diagonal had a length of 1.5 mm and the long diagonal had a length of 3 mm. The product had cracks in the coating; it was flaked off in some areas. The reject was about 25% of the area.

### Example 3

#### Anode Foil

20 To prepare an anode foil, 1.7 g of spheroidal graphite MCMB were mixed with 0.1 g of conductive carbon black (acetylene black), 0.2 g of polyvinylidene fluoride, copolymer (PVDF-HFP) and 2 g of acetone and processed into a uniformly dispersed paste in a cutting mixer. This paste was subsequently applied to a glass plate to form a foil with a doctor plate. A self-supporting foil, which was removed from the glass plate, was left behind after the evaporation of the solvent. The layer thickness of the dried layer was approx. 100 µm.

### Example 4

#### Cathode Foil

30 Corresponding to the anode foil, a cathode foil of equal size was prepared with the following composition: 3.6 g of LiCoO<sub>2</sub> were mixed with 0.2 g of conductive carbon black (acetylene black) and 0.2 g of PVDF as well as 4 g of acetone. Its layer thickness was likewise approx. 100 µm.

### Example 5

#### Separator Foil

40 1.5 g of a ceramic filler (lithium aluminum titanium phosphate) Li<sub>1.3</sub>Al<sub>0.3</sub>Ti<sub>1.7</sub>(PO<sub>4</sub>)<sub>3</sub> was processed with 0.5 g of PVDF-HFP and 2.4 g of acetone as described in (3) to prepare a separator foil with a thickness of about 50 µm.

### Example 6

#### Lamination

The electrode foils were laminated onto the particular collector grids in a roll type laminator. The foils were preheated to 160°C and then laminated under the roller with a

pressing force of 236 kp. The feed rate was 40 mm/sec. Subsequent tape tests showed good adhesion of the particular foils to the corresponding collector grids. The three elements, namely, the anode with the copper collector grid, the cathode with the aluminum collector grid and the separator foil, were laminated together in a second lamination step. The force was 16 kp, likewise at a lamination temperature of 160°C and a feed rate of 20 mm/sec. The design of the battery body is shown in Figures 1 and 2. Figure 1 shows a cross section through a battery body, while Figure 2 shows the top view of a battery body. Figure 1 shows the aluminum expanded metal (4) coated with adhesion promoter with the cathode foil (5) laminated to it and with the separator foil (6). The counterelectrode consists of copper expanded metal (8) coated with adhesion promoter with the anode foil (7) laminated to it. The aluminum expanded metal is seen in the top view in Figure 4. Two contact tongues (9) for contacting the body after packaging in foil are led out to the side.

15      **Example 7**

Manufacture of the Battery

The battery was introduced into a plastic-coated aluminum foil such that electric contacts were able to be led to the outside from the current collectors. A commercially available conducting salt solution LP30 was subsequently introduced into the laminated foil composite by absorption in a water-free protective gas atmosphere. The bag was then sealed hermetically. The battery was then formed and subsequently measured electrically. A good cycle life was found under a load with C rate. The curve is shown in Figure 4. More than 80% of the initial capacity was still present after 300 charge/discharge cycles.

The relative capacity of the battery was compared to that of a battery whose collector consisted of (error-free) coated expanded metal manufactured in the conventional manner. As is apparent from Figure 5, the performance data of the two batteries are essentially identical. The process according to the present invention consequently leads to coatings of the same quality as in the case of expanded metals coated in the usual manner.

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